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(11) **CA 2 115 639** (13) **C**

(40) 19.10.2004
(43) 04.09.1994
(45) 19.10.2004

(12)

(21) 2 115 639

(51) Int. Cl. 5: **B01J 31/18, C07C 11/107,
C07C 2/36**

(22) 14.02.1994

(30) 025,524 US 03.03.1993

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(54) TRIMERISATION DE L'ETHYLENE

(54) ETHYLENE TRIMERIZATION

(57)

Etthylene is trimerized to form 1-hexene by
using a catalyst comprising an aluminosilicate and
polydentate phosphine, arsine, and/or stibine
coordination complex of a chromium salt.



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CA 2115639 C 2004/10/19

(11)(21) **2 115 639**

(12) **BREVET CANADIEN
CANADIAN PATENT**

(13) **C**

(22) Date de dépôt/Filing Date: 1994/02/14

(41) Mise à la disp. pub./Open to Public Insp.: 1994/09/04

(45) Date de délivrance/Issue Date: 2004/10/19

(30) Priorité/Priority: 1993/03/03 (025,524) US

(51) Cl.Int.⁵/Int.Cl.⁵ B01J 31/18, C07C 2/36, C07C 11/107

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(54) Titre : TRIMERISATION DE L'ETHYLENE

(54) Title: ETHYLENE TRIMERIZATION

(57) Abrégé/Abstract:

Ethylene is trimerized to form 1-hexene by using a catalyst comprising an aluminoxane and polydentate phosphine, arsine, and/or silylene coordination complex of a chromium salt.

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ETHYLENE TRIMERIZATIONAbstract of the Disclosure

Ethylene is trimerized to form 1-hexene by using a catalyst comprising an aluminoxane and polydentate phosphine, arsine, and/or stibine coordination complex of a chromium salt.

ETHYLENE TRIMERIZATION

This invention relates generally to the oligomerization of ethylene and more specifically to the preparation of 1-hexene by the trimerization of ethylene using a catalyst which includes an aluminoxane and a chromium complex containing a coordinating polydentate phosphine, stibine or arsine ligand, such as a tridentate phosphine complex of a chromium salt.

Published European patent application, publication number 0,537,609, discloses an ethylene oligomerization/ trimerization process which uses a catalyst comprising a chromium complex which contains a coordinating polydentate ligand and an aluminoxane to produce high quality α -olefins which are enriched in 1-hexene. Suitable ligands include cyclic polyamines, and polypyrazolyl borates.

I have now found that certain polydentate ligand complexes of chromium salts in combination with aluminoxanes can catalyze ethylene oligomerization, and especially ethylene trimerization to form 1-hexene, with a very high degree of selectivity, e.g. about 95%.

In accordance with this invention there is provided a process for the trimerization of ethylene which process comprises reacting ethylene using a catalyst comprising an aluminoxane and a polydentate phosphine, arsine and/or stibine coordination complex of a chromium salt so as to form 1-hexene.

Also provided is an ethylene trimerization catalyst composition comprising an aluminoxane and a polydentate phosphine, arsine and/or stibine coordination complex of a chromium salt.

Aluminoxanes for use in the process of the invention can be prepared as known in the art by reacting water or water containing materials with trialkylaluminum

compounds in proportions of from 0.5 to 1.2 equivalents of water and, preferably, 0.8 to 1.0 equivalents of water per equivalent of trialkylaluminum. For example, Manyik et al U.S. 3,300,458 prepare alkylaluminosiloxane by passing a hydrocarbon solvent through water to form a wet hydrocarbon solvent and mixing the wet hydrocarbon solvent with an alkyl aluminum/ hydrocarbon solvent mixture in a conduit.

Schoenthal et al. U.S. 4,730,071 show the preparation of methylaluminosiloxane by dispersing water in toluene using an ultrasonic bath and then adding a toluene solution of trimethyl aluminum to the dispersion. Schoenthal et al U.S. 4,730,072 is similar except it uses a high speed, high shear-inducing impeller to form the water dispersion.

Edward et al. U.S. 4,772,736 describe an aluminosiloxane process in which water is introduced below the surface of a solution of hydrocarbon/ aluminum adjacent to a stirrer which serves to immediately disperse the water in the hydrocarbon solution.

The preparation of alkyl aluminosiloxanes from R_2AlOLi formed by reacting AlR_3 and anhydrous lithium hydroxide, and R_2AlCl has been reported in the literature, for example, Ueyama et al., Inorganic Chemistry, 12, No. 10, 2218 (1973) and Aoyazi et al., Inorganic chemistry, 12, No. 11, 2702 (1973).

Sinn et al. U.S. 4,404,344 prepare methylaluminosiloxane by adding trimethyl aluminum to a slurry of $CuSO_4 \cdot 5H_2O$ in toluene. Introducing water as a metal hydrate controls its reactivity with the trimethyl aluminum. Kaminsky et al. U.S. 4,544,762 is similar except it uses an aluminum sulfate salt hydrate to supply the water. Likewise, Welborn et al. U.S. 4,665,208 describe the use of other metal salt hydrates such as $FeSO_4 \cdot 7H_2O$ as a water source in preparing aluminosiloxane.

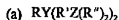
Hydrocarbonaluminosiloxanes may exist in the form of linear or cyclic polymers with the simplest compounds being a tetraalkylaluminosiloxane such as

tetraethylaluminum, $(C_2H_5)_4AlOAl(C_2H_5)_2$. Preferred aluminosiloxanes are prepared from trialkyl aluminum compounds such as triethyl aluminum, tri-n-butyl aluminum, triisobutyl aluminum, tri-n-hexyl aluminum, and tri-octyl aluminum. Of these, the more preferred are the compounds having C_6 or higher alkyl groups which have better solubility in the hydrocarbon solvent reaction medium. The aluminosiloxanes used to form the catalyst are preferably contained in organic solvents in concentrations of from 0.3 to 30 weight percent of total solvent plus aluminosiloxane.

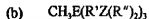
A trialkylaluminum compound can also be included in the catalyst (0.1 to 1.0 mole per mole of aluminosiloxane).

The chromium complexes which, upon mixing with an aluminosiloxane, catalyze ethylene oligomerization and especially trimerization in accordance with the process of the invention can be represented by the formula: $LCrX_n$, wherein L is a coordinating polydentate phosphine, arsine and/or stibine ligand and X represents anions which can be the same or different and n is an integer of 2 to 4. Such complexes can be in the form of oligomers, i.e. $(LCrX_n)_y$, where y is 2 to 8. By "polydentate" is meant that the ligand contains multiple donor atoms for coordination with chromium.

Preferred polydentate ligands include the following types:



wherein R and R'' are hydrogen or C_1 to C_{20} hydrocarbyl; R' is C_1 to C_{10} hydrocarbyl; and Y and Z are individually phosphorus, arsenic or antimony;



wherein E is C, Si, Ge or Sn and R', R'' and Z are as defined in (a) above;

(c) $E'(R'Z(R''))_3$

wherein E' is nitrogen, phosphorus, arsenic or antimony and R', R'' and Z are as defined in (a) above; and

(d) A-ZR-B

wherein A represents the number of atoms in the ring and is an integer of 9 to 18, B represents the number of Z atoms in the ring and is an integer of 3 to 6, R is a C₁ to C₁₀ alkyl group such as a methyl, ethyl, propyl, butyl, pentyl, hexyl or higher alkyl group or a C₆ to C₂₀ aromatic group such as benzyl and Z is phosphorous, arsenic or antimony. The abbreviations, such as 9-PR-3, 10-PR-3, 12-PR-4 and the like, used for the phosphine ligands correspond to those used for crown ethers because they are their phosphorus analogues. For example, 9-PR-3 denotes a nine membered ring with 3 phosphorus atoms. The most preferred coordinating polydentate ligands of this type are facially coordinating tridentate ligands such as 9-PMe-3.

In the ligands of types (a), (b) and (c) each (R'ZR'') moiety can be different so as to provide a mixture of donors in the same complex. The ligands of types (a), (b), (c), and (d) can be modified to attach to a polyethylene chain (m wt. = 1000 or higher) so that the resulting catalyst is homogeneous at elevated temperature but becomes heterogeneous at 25°C. This technique facilitates the recovery of the catalyst from the reaction products for reuse and has been used with other catalysts as described, for example, by D. E. Bergbreiter et al., *J. Chem. Soc., Chem. Commun.*, 337-338 (1985); *J. Org. Chem.*, (1986) 51, 4752-4760; and *J.A.C.S.* (1987), 109, 177-179.

Non-limiting examples of specific tridentate phosphine ligands include:

for type (a), $EtP(C_2H_4PEt)_2$, whose chemical name is bis-(2-diethylphosphinoethyl)ethylphosphine;

for type (b), $\text{CH}_3\text{C}(\text{CH}_2\text{PEt}_2)_2$, whose chemical name is 1,1,1-tris(diethylphosphinomethyl)ethane;

for type (c), $\text{P}(\text{C}_2\text{H}_4\text{PEt}_2)_3$, whose chemical name is tris(2-diethylphosphinoethyl)phosphine; and

- 5 for type (d), 9-PMe-3, whose chemical name is 1,4,7-trimethyl-1,4,7-triphosphino-cyclononane.

Other specific examples are:

- 10 $\text{CH}_3\text{C}(\text{CH}_2\text{PPh}_2)_3$
 $\text{PhP}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2$
 $\text{CyP}(\text{CH}_2\text{CH}_2\text{PCy}_2)_2$
 $\text{CyP}(\text{CH}_2\text{CH}_2\text{PEt}_2)_2$
 $\text{n-PrP}(\text{CH}_2\text{CH}_2\text{PEt}_2)_2$
 $\text{EtP}(\text{C}_3\text{H}_7\text{PEt}_2)_2$
 $\text{N}(\text{C}_2\text{H}_4\text{PEt}_2)_3$
 15 $\text{PhP}(\text{o-C}_6\text{H}_4\text{PEt}_2)_2$

wherein Ph = phenyl, Cy = cyclohexyl, Me = methyl, Et = ethyl and Pr = propyl. The arsine and stibine analogues of these ligands could also be prepared, for example:

- 20 $\text{PhAs}(\text{o-C}_6\text{H}_4\text{AsPh}_2)_2$
 $\text{MeAs}(\text{o-C}_6\text{H}_4\text{AsMe}_2)_2$
 $\text{MeSb}(\text{C}_2\text{H}_4\text{SbMe}_2)_2$
 $\text{MeAs}(\text{C}_3\text{H}_7\text{AsMe}_2)_2$

By a coordinating polydentate ligand is meant a ligand that sterically encumbers the chromium atom in such a way that the rate of chain propagation is decreased so that oligomerization, especially trimerization, rather than polymerization occurs. For example, ligands which occupy three adjacent coordination sites about an octahedral chromium atom.

Examples of suitable anions, X, include, but are not limited to, halides (Cl, Br, I, F), alkoxides (OR), carboxylates (O₂CR), and Oxo(O²⁻). These anions are initially the anion portion of the chromium compounds used to make the complex. The chromium in the compounds is initially in the oxidation state of II to VI and is preferably in the oxidation state of II, III or IV.

The chromium complexes can be prepared according to procedures set forth in the literature. For example L. R. Gray et al., J. Chem. Soc. Dalton. Trans. (1984), 47-53 and A. M. Arif et al. Inorg. Chem., Vol. 25, No. 8, 1986, 1080 - 1084.

The chromium complex and aluminoxane are combined in proportions to provide Al/Cr molar ratios of from 1:1 to 10,000 to 1 and, preferably, from 5:1 to 500 to 1. The amount of catalyst used is selected to provide the desired reaction rates at any particular reaction scale. (The presence of amounts of 0.001 mmole or more and preferably from 0.1 to 10 mmoles of chromium catalyst in a 300 ml reactor are effective to catalyze the reaction.) Catalyst mixing is preferably done at low temperatures of 0 to 35°C. The presence of ethylene during catalyst mixing at these temperatures resulted in no significant difference in catalyst properties when compared with catalysts prepared in the absence of ethylene. Ethylene provided a protective effect at temperatures above 55°C.

The reaction with ethylene is carried out in an inert solvent. Any inert solvent which does not react with aluminoxane can be used. The preferred solvents are aliphatic and aromatic hydrocarbons and halogenated hydrocarbons such as, for

example, toluene, xylene, ethylbenzene, cumene, mesitylene, heptane, cyclohexane, methylcyclohexane, 1-hexene, 1-octene, chlorobenzene, and dichlorobenzene. The amount of solvent is not particularly critical and generally ranges from 50 to 99 wt. percent of the initial reaction mixture.

- 5 Reaction temperatures and pressures are chosen to optimize reaction rates and selectivity. In general temperatures of from 35 to 200°C are used and preferably 80 to 120°C. Ethylene pressures can range from atmospheric to 3000 psig (20,786 kPa) and preferably from 100 to 1500 psig (791-10,444 kPa). Temperature and pressure affect reaction rate and purity in the following way: both higher temperature and
10 higher ethylene pressure increase reaction rate; higher ethylene pressures give better purity by forming less internal olefins, whereas higher temperatures increase the formation of internal olefins.

The invention is further illustrated by, but is not intended to be limited to, the following examples.

15 Example 1 - Preparation of Triphosphine Chromium Trichloride

Preparation of $n\text{-PrP}(\text{CH}=\text{CH}_2)_2$

- To a 1.0 M solution of vinylMgBr (70 mmol) in THF at 0°C was added a solution of $n\text{-PrP}(\text{CH}=\text{CH}_2)_2$ (3.75 g, 25.9 mmol) in 35 ml THF over $\frac{1}{4}$ hour. The solution was allowed to warm slowly and stirred overnight. To the resulting suspension was added degassed saturated NH_4Cl solution (50 ml) slowly to kill the unreacted
20 vinylMgBr. The organic phase was separated from the aqueous phase using a cannula. The remaining aqueous phase was washed with two 40-ml portions of Et_2O , which were then combined with the organic phase, dried over sodium carbonate and distilled at ambient pressure under inert atmosphere to give 2.0 g (60% yield) of $n\text{-PrP}(\text{C}_2\text{H}_5)_2$ (b.p. = 143°C).
25

Preparation of $n\text{-PrP}(\text{C}_2\text{H}_4\text{PEt}_2)_2$

A mixture of $n\text{-PrP}(\text{CH}=\text{CH}_2)_2$ (1.29 g, 10.0 mmol), Et_2PH (2.25 g, 25.0 mmol) and 2,2'-azobis(isobutyronitrile) (AIBN, 30 mg) in a closed flask under inert atmosphere was irradiated by a GE Sunlamp (275 W) one foot away for 24 hours.

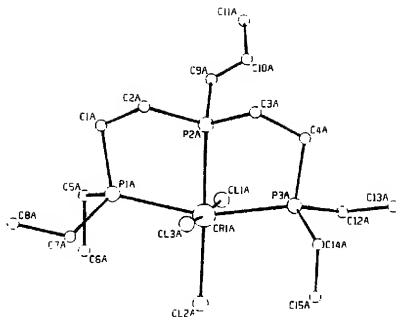
- 5 The resulting colorless liquid was stripped of volatiles under vacuum and vacuum distilled to give 3.1 g (97% yield) of product collected at 132-135°C/0.35 mmHg (46.7 Pa). ^{31}P -NMR (toluene): δ - 18.5 (2P); δ - 22.8 (1P).

Preparation of $[n\text{-PrP}(\text{C}_2\text{H}_4\text{PEt}_2)_2]\text{CrCl}_3$

- 10 A mixture of $n\text{-PrP}(\text{C}_2\text{H}_4\text{PEt}_2)_2$ (2.30 g, 7.46 mmol) and anhydrous CrCl_3 (0.40 g, 2.50 mmol) in a closed flask under vacuum was heated with stirring at 135°C for 1 hour. The reaction mixture at this stage contained four compounds: excess ligand (heptane-soluble), purple LCrCl_3 (toluene-soluble), blue LCrCl_3 (CH_2Cl_2 -soluble), and unreacted CrCl_3 . Separation was achieved by solubility difference. The resulting blue cake was extracted with 20 ml of toluene, filtered, and washed with
- 15 toluene until colorless. Toluene was removed from the combined purple filtrate, the residue was extracted with heptane, filtered to give a purple solid and unreacted ligand in heptane. The insoluble materials were a mixture of a blue solid and unreacted CrCl_3 . Separation was achieved by extraction with CH_2Cl_2 . Unreacted CrCl_3 (0.05 g) was recovered. Results: blue solid; 0.65 g, purple solid; 0.35 g. The combined yield
- 20 was quantitative based on reacted CrCl_3 . The blue and purple solids are both active in the ethylene trimerization reaction. Anal. for the blue compound, Calcd: P, 19.91; Cl, 22.79; Cr, 11.14; C, 38.60; H, 7.56. Found P, 19.77; Cl, 23.14; Cr, 11.46; C, 38.20; H 7.65.

The following diagram shows the structure of the product:

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Another ligand-chromium complex, $[\text{CyP}(\text{C}_2\text{H}_4\text{PEt}_2)_2]\text{CrCl}_3$, where Cy is cyclohexyl, was prepared analogously.

Example 2 - Ethylene Trimerization Reaction

- The reaction was carried out in a 300 ml Parr stainless-steel reactor to which a liquid addition bomb was connected for the purpose of adding the aluminoxane solution under ethylene pressure. To the reactor containing a solution of $[\text{n-PrP}(\text{C}_2\text{H}_4\text{PEt}_2)_2]\text{CrCl}_3$ (45 mg, 0.096 mmol) and pentadecane (0.267 g, as internal reference for gas chromatography) in 90 ml of toluene at 25°C under 250 psig (1825 kPa) of ethylene pressure was added a solution of n-hexylaluminoxane (5.0 mmol) in 10 ml of toluene using ethylene gas which brought the pressure to 300 psig (2197 kPa). The chain-growth reaction was then carried out with continuous ethylene feed at 95°C/610 (4302 kPa) psig for one hour (stirring rate: 800 RPM), during which time 22 g of ethylene was consumed. The reaction was terminated by pressing

methanol into the reactor to deactivate the catalyst. The reactor was cooled to 10°C, vented, and a sample was withdrawn for GC analysis which showed the following results: C₄: 4.3%, C₆: 94.3%, C₈: 0.2%, C₁₀: 0.9%. The purity of 1-hexene was 92.6% with major impurities being internal hexenes. The weights of the carbon
5 fractions were calculated using measured response factors and mimic experiments to simulate the operational loss of light olefins.

Results of this and other Examples 3-8 with varied reaction conditions are summarized in Table I.

Table I
Catalyzed Ethylene Trimerization Reactions¹

Example No.	Catalyst (mmol) ²		Pressure (kPa)	Temperature (°C)	Activity ³	Distribution (wt. %)				Purity (wt. %)
	Cr	Al				C ₄	C ₅	C ₆	C ₁₀	
2	.096	5.0	4307	95	8,200	4.1	94.3	.17	.64	92.6
3	.100	5.0	4376	80	3,200	3.1	94.4	.23	.52	94.4
4	.096	5.0	4928	115	11,100	9.6	89.3	.20	.65	87.4
5	.088	5.0	6789	94	17,000	3.2	94.9	.11	.59	93.7
6	.069	5.0	4307	106	7,800	8.6	90.3	.23	.62	90.0
(purple [n-PrP(C ₂ H ₅ PEt ₃) ₂]CrCl ₃)										
7	.084	6.0	4307	94	5,700	15.0	83.0	.13	.42	91.9
(propylaluminoxane was used)										
8	.097	10.0	4445	95	14,000	10.5	88.7	.38	.26	90.2
(blue [C ₂ P(C ₂ H ₅ PEt ₃) ₂]CrCl ₃ and butylaluminoxane were used)										

¹ Reactions were carried out in 100 ml toluene for one hour.

² Hexylaluminoxane and blue [n-PrP(C₂H₅PEt₃)₂]CrCl₃ were used unless otherwise noted.

³ Activity = mol ethylene/mol Cr/h.

CLAIMS:

1. A process for the trimerization of ethylene, said process comprising reacting ethylene, using a catalyst comprising an aluminoxane and at least about 0.001 mmole of a polydentate phosphine, arsine, and/or stibine coordination complex of a chromium salt, wherein said coordination complex has the formula $LCrX_n$, wherein L is a coordinating polydentate phosphine, arsine and/or stibine ligand, X represents anions which can be the same or different, and n is an integer from 2 to 4.

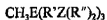
2. A process for the trimerization of ethylene, said process comprising reacting ethylene, at a temperature of from about 35°C to about 200°C and an ethylene pressure of from about atmospheric to 3000 psig, using a catalyst comprising an aluminoxane and at least about 0.001 mmole of a polydentate phosphine, arsine, and/or stibine coordination complex of a chromium salt, wherein said coordination complex has the formula $LCrX_n$, wherein L is a coordinating polydentate phosphine, arsine and/or stibine ligand, X represents anions which can be the same or different, and n is an integer from 2 to 4.

3. The process according to claim 2 wherein said polydentate ligand has the formula:



wherein R and R'' are hydrogen or C₁ to about C₂₀ hydrocarbyl; R' is C₁ to about C₁₀ hydrocarbyl; and Y and Z are individually phosphorus, arsenic or antimony.

4. The process according to claim 2 wherein said polydentate ligand has the formula:



wherein E is C, Si, Ge or Sn; R' is C₁ to about C₂₀ hydrocarbyl; each R'' is individually hydrogen or C₁ to about C₁₀ hydrocarbyl and each Z is individually phosphorus, arsenic or antimony.

5. The process according to claim 2 wherein said polydentate ligand has the formula:



wherein E' is nitrogen, phosphorus, arsenic or antimony; R' is C₁ to about C₂₀ hydrocarbyl; each R'' is individually hydrogen or C₁ to about C₁₆ hydrocarbyl and each Z is individually phosphorus, arsenic or antimony.

6. The process according to claim 1 wherein said polydentate ligand is a ring which has the formula:



wherein A represents the number of atoms in the ring and is an integer of 9 to 18, B represents the number of Z atoms in the ring and is an integer of 3 to 6, R is a C₁ to C₁₆ alkyl or a C₆ to C₂₀ aryl group and Z is phosphorus, arsenic or antimony.

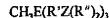
7. An ethylene trimerization catalyst composition comprising an aluminoxane and at least about 0.001 mmole of a polydentate phosphine, arsine, and/or stibine coordination complex of a chromium salt, wherein said coordination complex has the formula $LCrX_n$, wherein L is a coordinating polydentate phosphine, arsine and/or stibine ligand, X represents anions which can be the same or different, and n is an integer from 2 to 4.

8. The catalyst composition of claim 7 wherein said polydentate ligand has the formula:



wherein R and R'' are hydrogen or C₁ to C₂₀ hydrocarbyl; R' is C₁ to C₁₆ hydrocarbyl; and Y and Z are individually phosphorus, arsenic or antimony.

9. The catalyst composition of claim 7 wherein said polydentate ligand has the formula:



wherein E is C, Si, Ge or Sn; R' is C₁ to C₂₀ hydrocarbyl; each R'' is individually hydrogen or C₁ to C₁₀ hydrocarbyl and each Z is individually phosphorus, arsenic or antimony.

10. The catalyst composition of claim 7 wherein said polydentate ligand has the formula:



wherein E' is nitrogen, phosphorus, arsenic or antimony; R' is C₁ to C₂₀ hydrocarbyl; each R'' is individually hydrogen or C₁ to C₁₀ hydrocarbyl and each Z is individually phosphorus, arsenic or antimony.

11. The catalyst composition of claim 7 wherein said polydentate ligand is a ring which has the formula:



wherein A represents the number of atoms in the ring and is an integer of 9 to 18, B represents the number of Z atoms in the ring and is an integer of 3 to 6, R is a C₁ to C₁₀ alkyl or a C₆ to C₂₀ aryl group and Z is phosphorus, arsenic or antimony.